NEW METHOD FOR THE SYNTHESIS OF SUBSTITUTED 1,4-DIHYDROPYRAZINES

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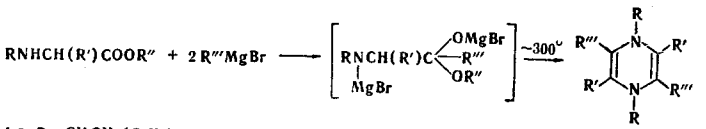
We have found that the previously inaccessible hexaalkyl-1,4-dihydropyrazines and other N,N'-dialkyl-1,4-dihydropyrazines can be obtained by thermolysis of the products of reaction of α-(alkylamino)carboxylic acid esters with alkylmagnesium bromides:



1a $R = CHCH_3(C_2H_5)$, $R' = CH_3$, $R''' = C_2H_5$;
1b $R = CH_2(CH_2)_2CH_3$, $R' = H$, $R''' = C_2H_5$

1a, b

When ethyl α-sec-butylaminopropionate was added to an ether solution of 2 moles of ethylmagnesium bromide, 1 mole of ethane was evolved, and an ether-insoluble compound was formed; the solvent was removed, and the ether-insoluble compound was heated in vacuo (1 ml) to 250-300°. The resulting liquid distilled along with the contents of the trap. Workup gave 2,5-dimethyl-3,6-diethyl-1,4-di-sec-butyl-1,4-dihydropyrazine (Ia) (49%) with bp 82° (27 mm), d_4^{90} 0.8106, and n_D^{20} 1.4386. The IR spectrum contains an absorption band at 1665 cm^{-1} (C=C). PMR spectrum: 1.15 (24 H, CH_3), 1.75 (8 H, CH_2), and 3.45 ppm (2 H, NCH). An intense singlet ESR signal develops under the influence of p-chloranil (see [1]). Found: C 77.8; H 12.7; N 10.1%; M 271 (cryoscopically); MR_D 90.07. $C_{18}H_{34}N_2$. Calculated: C 77.6; H 12.3; N 10.1%; M 278; MR_D 90.15.

3,6-Diethyl-1,4-di-n-butyl-1,4-dihydropyrazine (Ib) (48%), with bp 70° (10 mm), d_4^{20} 0.8084, and n_D^{20} 1.4355, was similarly obtained from ethyl α-butylaminoacetate and ethylmagnesium bromide. Its IR spectrum contains a band at 1670 cm^{-1} (C=C). PMR spectrum: 1.05 (12H, CH_3), 1.55 (12H, CH_2), and 2.55 ppm (4H, NCH). Found: C 76.9; H 12.2; N 10.9%; MR_D 80.83. $C_{16}H_{30}N_2$. Calculated: C 76.7; H 12.2; N 11.1%; MR_D 80.91.

LITERATURE CITED

1. J. W. Lown and M. H. Akhtar, Chem. Commun., No. 14, 829 (1972).

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